Analysis of effluent discharged into <u>Hamilton Harbour</u> for polynuclear aromatic hydrocarbons

May 1978

Ontario. Ministry of the Environment

MOE HAM ANA ATAA

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OTC REPORT 7809

ANALYSIS OF EFFLUENTS

DISCHARGED INTO HAMILTON HARBOUR

FOR POLYNUCLEAR AROMATIC HYDROCARBONS

by

R. D. Smillie, D. Robinson and D. T. Wang

Ministry of the Environment

Organic Trace Contaminants Section

Laboratory Services Branch

May, 1978

MOE HAM ANA ATAA

ataa

### ABSTRACT

Seven samples of effluents that are discharged into Hamilton Harbour were analyzed for polynuclear aromatic hydrocarbons (PAHs). All the samples were found to contain PAHs, with the highest concentration being found in the sample of Stelco's weak ammonia liquor discharge. Approximately 40 PAHs were identified by gas chromatography/mass spectrometry including numerous heterocyclic aromatic hydrocarbons.

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### 1. INTRODUCTION

Polynuclear aromatic hydrocarbons (PAHs) occur widely in the environment and can originate from a number of sources. Recent studies have shown PAHs to be present in the body lipids of adult Herring Gulls taken from Lake Ontario<sup>1</sup>. Also PAHs have been shown to be prevalent in Lake Ontario sediments<sup>2</sup>. As Herring Gulls are fish-eating birds, and are known to bioaccumulate pollutants from their diet, carp and pike were taken from Hamilton Harbour and analyzed for PAHs. These results have been reported elsewhere<sup>3</sup>, and were generally in range between 20-300 ng/kg for perylene, benzo(k)-fluoranthene, benzo(a)pyrene and coronene.

Because of the PAHs found in these fish the Laboratory Services Branch was requested to analyze some of the effluents that are discharged into Hamilton Harbour for PAHs.

#### 2. SAMPLES

Samples were received April 20th, 1978.

Senders No.	Lab. No.	Description					
1	OX16-1	Hamilton STP effluent Composite 600-1200, April 19/78.					
2	OX16-2	Stelco-West Side Open Cut Composite 830-1100, April 19/78.					
3	OX16-3	Stelco-North Trunk Sewer Composite 830-1100, April 19/78.					

Senders No.	Lab. No.	Description				
4	OX16-4	Stelco-Coke Side Shed Precipitator Effluent, Composite 830-1100, April 19/78.				
5	OX16-5	Stelco-Weak Ammonia Liquor to Sanitary Sewer Composite 830-1100, April 19/78.				
6	OX16-6	Dofasco-Blast Furance Cooling Water Sewer. Composite 1130-1500, April 19/78.				
7	OX16-7	Dofasco-Coke Plant Melt Shop Sewer. Composite 1130-1500, April 19/78.				

It should be noted that sample OX16-5 was approximately  $30^{\rm O}$  when it arrived, and some pressure was released when it was opened.

### 3. EXPERIMENTAL

#### 3.1 Apparatus

## 3.1.1 Liquid Chromatography

A Varian Model 8500 Liquid Chromatograph equipped for gradient elution was used. A variable wavelength Varian Varichrom Spectrometer was coupled to a Schoeffel FS-970 fluorescence detector. The column outlet was coupled to the detectors by means of 0.25 mm I.D. stainless steel tubing.

## 3.1.2 Gas Chromatography

A Varian 3700 gas chromatograph equipped with a flame ionization detector was used.

### 3.2 Columns

## 3.2.1 Liquid Chromatography (HPLC)

A Vydac 201 TP column (The Separation Group) was used. This is a reverse phase column.

## 3.2.2 Gas Chromatography

A Dexsil 300 100/120 mesh column was used. This was glass, 1.8 m  $\times$  2 mm I.D., and connected to the gc with Vespel ferrules.

#### 3.3 Reagents

Spectrograde acetonitrile was obtained from Burdick and Jackson Inc. Cyclohexane, (distilled-in-glass) and benzene (distilled-in-glass) were obtained from Caledon Laboratories Ltd. PAH standards used in this study were from the following suppliers: pyrene, benzo(e)pyrene (BeP), perylene (PER) and benzo(g,h,i)-perylene (BghiP) from Aldrich Chemical Co.; benzo(a)-pyrene (BaP) and dibenz (a,h)anthracene (DBahA) from Eastman Kodak Co.; chrysene and fluoranthene from J. T. Baker Chemical Co.; benzo(k) fluoranthene (BkF) from J. L. Monkman, Environment Canada; o-phenylenepyrene (OPP) and anthanthracene (AA) were obtained from F. I. Onuska, CCIW, Burlington, Ontario.

# 3.4 Operating Conditions

## 3.4.1 Liquid Chromatography (HPLC)

The eluent was a mixture of acetonitrile (75%) and water (25%, V/V) applied at a pressure of  $105 \text{ Kg/cm}^2$  and a flow rate of 1.0 ml/min.

The separation of the synthetic mixture of PAHs and those from environmental samples were both performed under these conditions at ambient temperature. Occasionally, the column was regenerated by the elution of acetonitrile.

In analyses where the wavelengths were varied, the UV detector was monitored at 240 nm (for fluoranthene and pyrene), and 295 nm (for BkF, BaP, DBahA, and BghiP). The fluorescence detector was set at  $\lambda_{\rm excitation} = 254$  nm,  $\lambda_{\rm emission} > 370$  nm (for fluoranthene, chrysene, DBahA and BghiP), and  $\lambda_{\rm excitation} = 240$  nm,  $\lambda_{\rm emission} > 370$  nm (for perylene, BkF and BaP). The baselines were adjusted as necessary after changing detector wavelengths  $\lambda_{\rm excitation} = 240$  nm,

## 3.4.2 Gas Chromatography

An injector temperature of  $200^{\circ}$ , and a detector temperature of  $300^{\circ}$  were used. The carrier gas was helium, and was set at 30 mL/min. The starting temperature,  $100^{\circ}$ , was held for 4 minutes, and then programmed to  $300^{\circ}$  at  $6^{\circ}$ /minute.

# 3.5 Identification and Quantitation of PAHs

## 3.5.1 Liquid Chromatography (HPLC)

The separated PAHs were identified by retention and their specific ultraviolet and/or fluorescence responses as compared with those of standards. Quantitative analyses were obtained by comparing the HPLC peak height with that of a standard calibration curve constructed for each PAH.

### 3.5.2 Gas Chromatography

The separated PAHs were identified by retention time and by peak area as compared to standards as determined by the Varian CDS-111 data acquisition system.

## 3.5.3 Gas Chromatography/Mass Spectrometry

A DuPont 21-491B gc/ms system was used. The glass column was a Dexsil 300, 100-120 mesh, 2.0 m x 3 mm I.D. The column flow rate was 20 mL/min. The injector and detector temperatures were 225° and 235° respectively. The column temperature was 100° and held for 4 minutes, then programmed at 6°/minute to 300°. The mass spectra were automatically acquired on the DS50S data system.

#### 3.6 Extraction Procedure

#### 3.6.1 General

The aqueous samples (750 mL) were first extracted with 100 mL of benzene, then again with two 50 mL portions of benzene. The organic extract was then dried with preextracted sodium sulphate, and concentrated.

#### 3.6.2 Liquid Chromatography

Samples OX16-1,2,3, and 6 were carefully evaporated to near dryness, then made up to 1.0 mL with acetonitrile/water.

A portion of samples OX16-4,5 and 7 (usually 20%) was carefully evaporated to near dryness then made up to 1.0 mL with acetonitrile/water.

### 3.6.3 Gas Chromatography

Only samples OX16-4,5 and 7 were analyzed by gas chromatography. A pertion of these samples (usually 10%) was concentrated to near dryness and the organic extract was then made up to 1.0 mL with cyclohexane.

#### 3.6.4 Gas Chromatography/Mass Spectrometry

Only samples OX16-4,5 and 7 were analyzed by gc/ms. A portion of the sample (usually 10%) was concentrated to 0.1 mL.

When sample OX16-7 was being concentrated, some crystal precipitated out of solution. These crystals were removed and are currently being analyzed separately.

## 4. RESULTS

# 4.1 Gas Chromatography/Mass Spectrometry

Approximately 40 polynuclear aromatic hydrocarbons (PAHs) were identified in the samples submitted for analysis. Many of these compounds were heterocyclic.

Table 1 lists the PAHs that were identified in the three samples (OX16-4, 5 and 7) that were submitted for gc/ms analysis. The structures of these compounds can be found in 7.1 (Appendix 1).

Table 2 lists the heterocyclic polynuclear aromatic hydrocarbons with organic-bound nitrogen. The structures of these compounds can be found in 7.2 (Appendix 2).

Table 3 lists the oxygen containing polynuclear aromatic hydrocarbons. The structure of these compounds can be found in 7.3 (Appendix 3).

One sulphur containing heterocycle was identified and this compound is listed in Table 4. The structure of this compound can be found in 7.4 (Appendix 4).

## 4.2 Gas Chromatographic Analysis

The most predominant compounds identified by gc/ms were quantitated. These are listed in Table 5. The relative response was calculated for compounds with the same number of rings, i.e. the response factor for chrysene (4 rings) was used for benzanthracene (4 rings) and pyrene (4 rings). The major components in sample OX16-5 were phenolic, and the response factor used was phenol.

TABLE 1

PAHS IDENTIFIED IN SAMPLES

	<u>OX16-4</u>	OX16-5	<u>0X16-7</u>
Naphthalene		х	X
Methylnaphthalene			х
Bipheny1		X	х
Dimethylnaphthalene			х
Acenaphthylene		x	x
Acenaphthene			Х
Fluorene		x	х
Anthracene	x	X	x
Phenanthrene	х	X	X
Fluoranthene	X	х	x
Pyrene	X	X	X
Benzanthracenes	X	X	X
Benzopyrenes	X	X	X
Benzofluoranthenes	Х	X	X
Methylphenanthrene	x		
Dimethy1phenanthrene	X		
Benzofluorenes	x	X	X
Chrysene	Х	X	x
Methylchrysenes	X		
Dimethylchrysenes	X		
Benzoperylenes	X	Х	X
Methylbenzanthracene	х		
Dibenzanthracene	x	X	x
Methylbenzopyrenes		<b>`</b> x	
Anthanthrene	x	x	x
Indenopyrene	x	х	Х

TABLE 2

NITROGEN CONTAINING HETEROCYCLES

	OX16-4	OX16-5	OX16-7
Quinolines		X	
Methylquinolines		X	
Indole		X	Х
Methylindoles		х	
Carbazole		х	
Methy1carbazole		X	
Benzindoles		X	
Acridines		X	

TABLE 3

OXYGEN CONTAINING HETEROCYCLES

	OX16-4	OX16-5	OX16-7
Benzofuran		X	
Methylbenzofuran		X	
Dibenzofuran		X	X
Naphtho1s		X	
Methylnaphthols		x	
Fluorenone	9)	х	

# TABLE 4

# SULPHUR CONTAINING HETEROGYGLES

Naphthothianaphthene

Sample OX16-4

QUANTITATION OF THE MAJOR ORGANICS

PRESENT IN THE EFFLUENTS

mg/L

SAMPLE				
OX16-4	OX16-5	OX16-7		
	100			
	7.2			
	14			
	110	.37		
	172			
	140			
	25	.38		
		.08		
.18	13	.36		
	25			
		.30		
.28	5	.05		
. 22	3	.05		
.03				
.04				
	.18	OX16-4     OX16-5       100     72       14     110       172     140       25       .18     13       25       .28     5       .22     3       .03		

TABLE 6

QUANTITATION OF PAHS BY HPLC

## CONCENTRATION ug/L

SAMPLE	PER	BkF	ВаР	DBahA	BghiP	OPP	AA	COR
OX16-1	.02	.02	.03	nd	.22	.30	.09	.15
OX16-2	.09	.04	.11	nd	.34	.28	0.12	.11
OX16-3	.34	.20	.52	nd	.93	1.0	.32	.22
OX16-4	7.6	5.4	11.0	5.0	20.	24	6.90	3
OX16-5	17.8	8.6	30	10	52	66	28.	14
OX16-6	.06	.03	.11	nd	.40	.28	.15	.10
OX16-7	2.0	1.0	4.0	nd	7.8	9.6	3.6	1.8

detection limit .01 ug/L for PAHs in Table 6.

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## 4.3 Liquid Chromatographic Analysis

Ten PAHs that are extremely difficult to chromatograph by gas chromatography are routinely analyzed by liquid chromatography, using fluorescence and ultraviolet detectors in series.

The results obtained for these analyses are given in Table 6.

#### 5. DISCUSSION

The number of aromatic compounds that were identified (and quantitated) is not really surprising considering that coking of coal is involved.

The weak ammonia liquor (OX16-5), which is assumed to be the aqueous condensate in the coking process (ammoniacal liquors) did indeed contain a large number of heterocyclic polynuclear aromatic hydrocarbons. These were also highly concentrated in the sample. Although pyridine and picotines would have been expected, it may be that these compounds were probably too close in retention time to the solvent to be identified. The sample (OX16-5) smelled strongly of phenolics, and these compounds were indeed predominate as determined by gc analysis.

Samples OX16-4 had lower concentrations of PAHs and contained very little PAHs of the volatile nature.

Sample OX16-7 contained the full range of PAHs, but very few heterocyclic compounds.

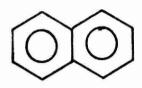
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- D. J. Hallett, R. D. Smillie, D. T. Wang, F. I. Onuska, M. E. Comba and R. Sonstegard. Int'l Symp. Analysis of Hydrocarbons and Halogenated Hydrocarbons, Hamilton, Ontario, May 1978.
- 4. R. D. Smillie, D. T. Wang and O. Meresz, J. Environ. Sci. Health, Al3, 47 (1978).

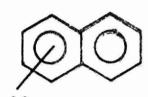
# 7. APPENDICES

# 7.1 Appendix 1

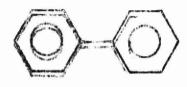
Structures of compounds listed in Table 1.



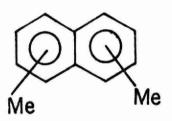
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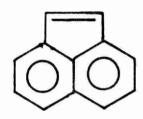
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Bipheny1



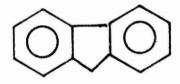
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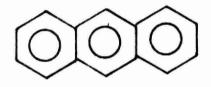
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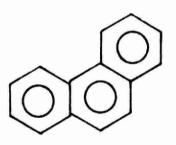
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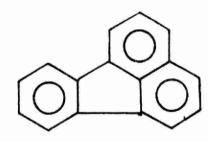
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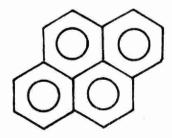
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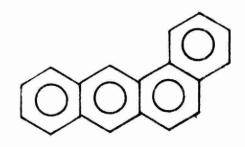
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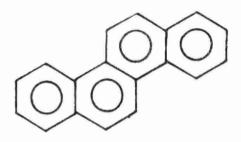
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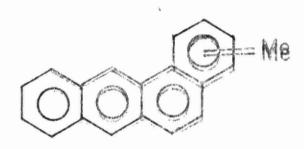
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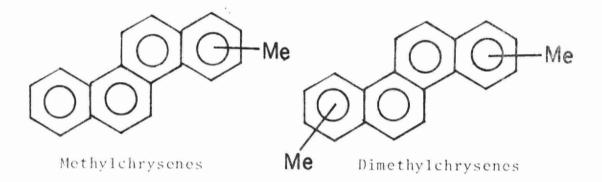
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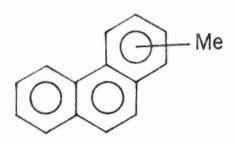


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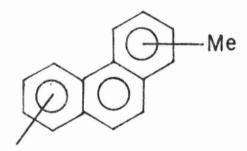


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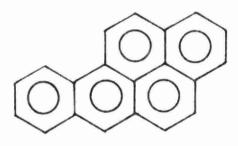




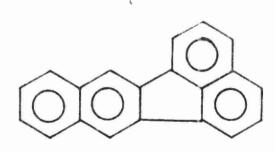
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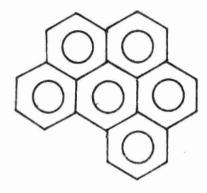
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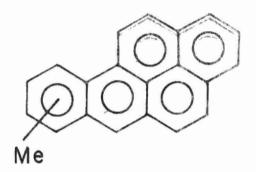
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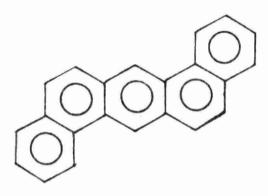
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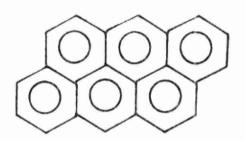
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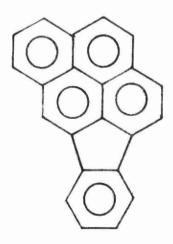
Methylbenzopyrenes



Dibenzanthracenes



Anthanthrene



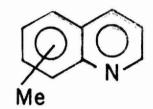
Indenopyrenes

# 7.2 Appendix 2

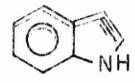
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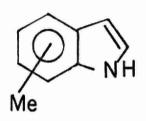
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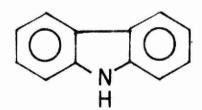
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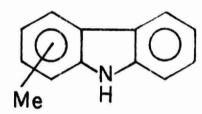
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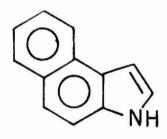
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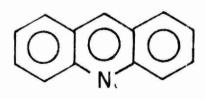
Carbazole



Methylcarbazoles



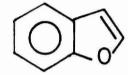
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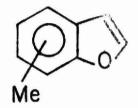


Acridine

# 7.3 Appendix 3

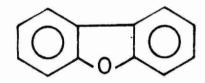
Structures of compounds listed in Table 3.





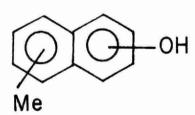
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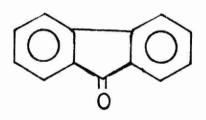
Methylbenzofuran



Dibenzofuran

Naphtho1s



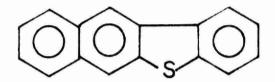


Methylnaphthols

Fluorenone

# 7.4 Appendix 4

Structure of the compound listed in Table 4.



Naphthothianaphthene

•

• • •

7530 - 1239 Letter size - 1/2 cut tab

Ontario Ontario

MOE/HAM/ANA/ATAA
Smillie, R.D.
Analysis of
effluents discharged ataa
into Hamilton c.1 a aa
Harbour for polynuclear...

